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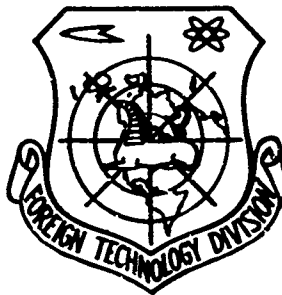
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MATTING OF ALUMINUM AND ITS ALLOYS

By

S. I. Shames



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MATTING OF ALUMINUM AND ITS ALLOYS

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ABSTRACT: The report covers a study of film formation kinetics and the properties of anodic oxide films produced in an oxalic acid electrolyte with the titanium salt $TiO(KC_2O_4)_2 \cdot 2H_2O$ on aluminum AD-1 and Al alloys

AMtsM and D16-T (unclad). Samples were wiped with benzine, chemically degreased (bath compositions given, 3 min., 60-70C for unpolished and 3-5 min., 70-80C for polished samples), hot and cold water rinsed, bleached (1-2 min., 40-50% HNO_3 , 18-20C), then anodized (bath composition given). The optimal conditions were 55C and 40 min. at 2 a/dm^2 or 30 min. at 3 a/dm^2 . Corrosion resistance was high and increased with process duration. Increasing the pH to a value of 3 did not affect film quality. Corrosion resistance, abrasive and friction wear, hardness, volume resistivity and dielectric strength characteristics of these films were better than for standard oxide films produced in sulfate or oxalate baths. English Translation: 14 pages.

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, Ъ; e elsewhere.
 When written as ѣ in Russian, transliterate as y^ě or ѣ.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

MATting OF ALUMINUM AND ITS ALLOYS

S. I. Shames

Oxide films obtained on aluminum and its alloys during oxidizing possess high stability in conditions of atmospheric corrosion; good electrical insulating properties, resistance to wear by abrasion, and heat-insulating ability. A colored oxide film is used for decorative finishing of various widely-used articles and architectural constructions. The high physicomachanical properties of contemporary aluminum alloys in combination with the above-enumerated properties of oxide films permit their successful application in many branches of technology.

There is no doubt that oxide films on aluminum are very promising and that with further study the area of their application will be expanded.

This work concerns an investigation of the kinetics of growth and the properties of opaque anodic and oxidized films (oxide films) obtained in oxalic acid electrolyte containing a titanium salt. The obtaining of opaque oxide films is characterized by the following peculiarities: a) oxidizing (matting) and pigmentation proceed simultaneously in one working process; b) to improve the quality of the oxide film and to give it an enamel-like appearance inorganic substances, salts of

titanium, thallium, or zirconium) are introduced into the film. Finely-dispersed hydroxides of titanium or zirconium introduced into the electrolyte fill the pores in the film and, being introduced into it, give it the appearance of an opaque enamel-like coating of light-gray to milk-white color depending upon the alloy anodized and the duration of matting.

It has not been excluded also that the opacity of a mat-film is partially explained by its individual structure (see p. 204 of this collection of reports).

The investigation was conducted on 80 x 15 x 2 mm samples from the materials AD-1, AMtsM, and D16-T.

Technology and Kinetics of the Process

The approximate flow chart of matting of a sample consists of the following operations: polishing, degreasing, washing in hot and cold water, brightening, washing in cold running water, drying, matting, washing airtightening, and drying. In industrial conditions for decorative finishing polishing on a clean coarse calico wheel is done.

Mat-films are opaque and therefore conceal the metallic base. This means that thorough preparation of the surface need not be carried out. Therefore such labor-consuming processes as mechanical and electrical polishing can be omitted from the technological process without damaging the quality of the article. For the production of brilliant matted films intended for decorative purposes one should carry out mechanical polishing of the parts, using a paste with an aluminum oxide base.

Degreasing is conducted in an organic solvent (gasoline) by rubbing the samples with rags. The best results are obtained by

degreasing with the use of ultrasonics in the same solvent.

Chemical degreasing is done in a solution of the following composition:

tribasic sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) - 40-50 g/liter;

sodium hydroxide (NaOH) - 40-50 g/liter;

soluble glass [sodium orthosilicate] (Na_2SiO_3) - 25-30 g/liter.

Temperature of solution: $60-70^\circ$; time of holding, 3 minutes.

Polished components can be degreased with Viennese lime of in a solution of the composition:

sodium carbonate (Na_2CO_3) - 50-60 g/liter;

soluble glass (Na_2SiO_3) - 25-30 g/liter;

liquid soap - 3-5 g/liter.

Temperature of solution: $70-80^\circ$; time of holding: 3-5 minutes.

After degreasing the samples are thoroughly washed in hot and then in cold running water.

Brightening is produced in a 40-50% solution of nitric acid at a temperature of $18-20^\circ$ with submersion of the sample in the solution for 1-2 minutes, with subsequent washing in cold running water and drying at a temperature of $80-90^\circ$.

Oxidizing is conducted in various solutions; however, the best indices were found in oxide-film obtained in a solution of the following composition:

titanium-potassium oxalate, $\text{TiO}(\text{KC}_2\text{O}_4)_2 \times 2\text{H}_2\text{O}$ of the plant "Red chemist," Leningrad, 50 g/liter;

boric acid (H_3BO_3) - 10 g/liter;

citric acid ($\text{C}_6\text{H}_8\text{O}_7$) - 1 g/liter;

oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) - 1.2 g/liter.

The electrolyte was prepared in distilled water heated to 50° in the order shown in the recipe.

Oxidizing was conducted in a glass bath with a capacity of 4 liters; it was installed in a thermostat. As cathodes we used carbon plates placed in capron cases; the electrolyte was energetically mixed by mechanical mixers. The assigned temperature was maintained by pumping cold water through a glass coil placed on the bottom of the bath. The experiments were conducted at various current densities and electrolyte temperatures.

After oxidizing, the samples were washed in running water, airtightened in boiling water, in which they were held for 30 minutes, and then dried at a temperature of 100° .

Figure 1 presents the growth curves of mat-film as functions of the duration of oxidation at various current densities. Analysis of these curves shows that here, as also during ordinary anodizing in oxalic acid, there are sections where a linear dependence between the growth of the film and the duration of the process is observed.*

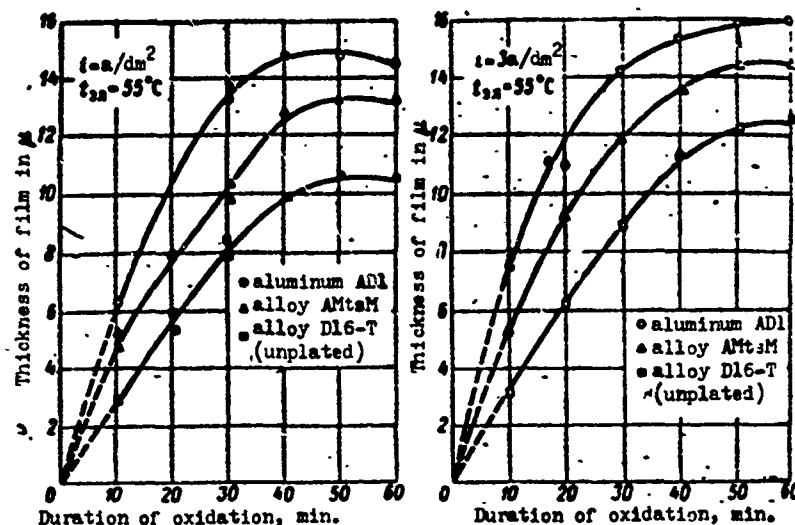


Fig. 1. Curves of the dependence of the thickness of the mat-film (δ) on the duration of oxidizing (τ) at various current densities.

*Thickness of mat-film was determined by the weight method and with the ET-1A instrument, working on the principle of eddy currents.

However, after 40 minutes of oxidizing at a current density of current 2 a/dm^2 (and 30 minutes at a current density of 3 a/dm^2) the rate of growth of the film decreases. This phenomenon is obviously connected with certain peculiarities of the forming of the oxide-film.

As our investigations show, the film formed on the checked alloys is very dense (Fig. 2) and the penetration of the electrolyte into the depths of its pores is more hampered

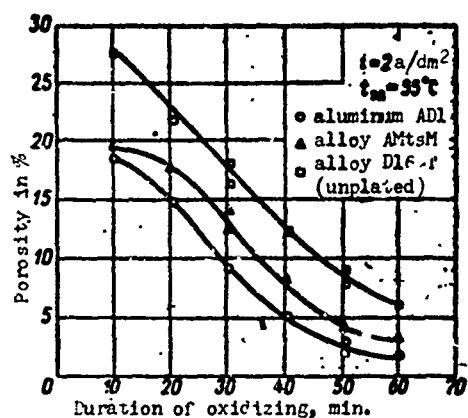


Fig. 2. Curves of the dependence of porosity of a mat-film on the duration of oxidizing (τ).

than in the case of films obtained with the usual process. With an increase in current density there appears in the electrolyte intense formation of a finely-dispersed hydroxide of titanium and the filling of the pores of the growing film by it proceeds faster. Besides this, part of the volume of pores is filled with electrolyte and gaseous products of

electrolysis. This leads to a situation in which at a large current density a discharge, accompanied by sparking appears on the anode. The current drops catastrophically, and voltage grows. This is the region of unregulated regimes of the bath. Discharges on the anode delay film growth and lead to its partial surface destruction. Thus the optimum time of forming a mat-film at a constant current density of 2 a/dm^2 is 40 minutes and that at a constant current density of 3 a/dm^2 is 30 minutes. The end voltage in the bath oscillated within the limits 110-140 v. If a constant current density is not maintained, voltage grows rapidly from 60 to 120 v and remains constant, while current density drops from the assigned value to $0.7-0.8 \text{ a/dm}^2$. Apparently it is possible to oxidize all alloys of aluminum under

the indicated conditions.

Corrosion Resistance of Mat-Film

As was shown above, the corrosion resistance of a mat film is very high. The film is insensitive to the action of alcohol and the acetone ester of hydrogen peroxide and also is neutral to the action of food products [1].

The corrosion resistance of anodized films on aluminum can be evaluated by the [VIAM] (BNAM)* test [2]; however, this test in its usual form turned out to be ineffective for mat films, owing to the duration of the test (time for a drop to turn green reached 60-90 minutes with its repeated renovation). The high value of the time of greening of a drop is connected with the increased density of the film and the filling of its pores by titanium hydroxide. Therefore we applied another method (accelerated) for appraisal of the corrosion resistance of mat films.

A potential of 8 v from an a-c source was applied through platinum electrodes to the test specimen and to a drop of VIAM solution placed on it. The alternating electric field which appeared promoted penetration of the VIAM solution into the pores to the base metal. This enabled us to reduce the time for greening of a drop of VIAM solution to 5-25 minutes, i.e., to accelerate test time by 5-7 times. The accelerated VIAM method is unsuitable for the usual sulfuric or oxalic acid film, since it gives an instantaneous effect.

Figure 3 gives curves of the change in the corrosion resistance of oxide-films, depending upon the duration of oxidizing. The rapid

*All-Union Scientific Research Institute of the Science of Aviation Materials. [Trans. Ed. Note]

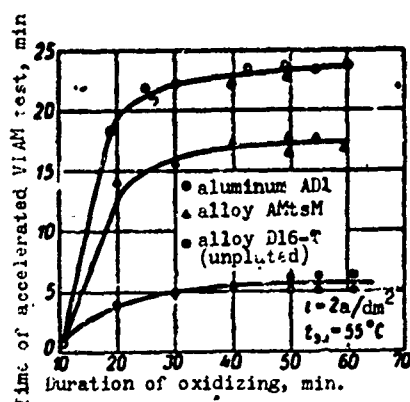


Fig. 3. Curves of the dependence of corrosion resistance of mat films on the duration of oxidizing (τ).

growth of the corrosion resistance of mat film with time is explained by the filling of its pores by finely-dispersed titanium hydroxide and the considerable introduction of the latter directly into the structure of the film.

Influence of Electrolyte Temperature on the Growth of Mat Films

The curves of the dependence of the thickness of mat film on the duration of oxidizing of the electrolyte for alloy AD1 are presented in Fig. 4, from which one can see that the formation of the film occurs suffi-

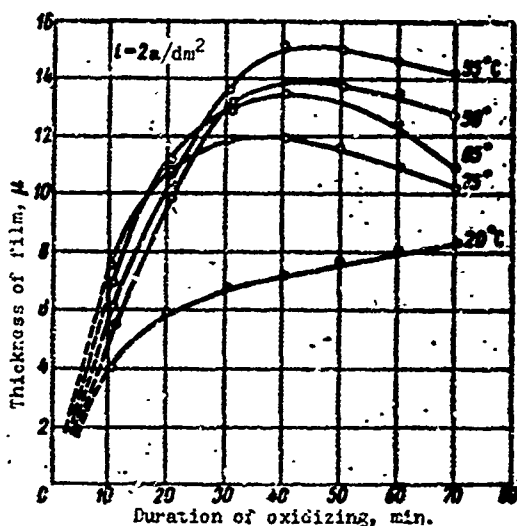


Fig. 4. Curves of the dependence of film thickness (δ) on the duration of oxidizing (τ) and the temperature of the electrolyte for the alloy AD1.

ciently fast even with the bath at room temperature (20°). However, the best conditions for film growth are created at a temperature of 55° which should be considered optimum for the given process. At higher electrolyte temperatures during the first twenty minutes the oxidizing curves almost coincide with the optimum curve of oxidizing (55°), but then the rate of growth of the film falls rapidly. This is explained by the increase in the

dissolving action of the electrolyte with an increase in its temperature and also by the more intense formation of titanium hydroxide and its precipitation in the pores of the film. The latter is confirmed by the fact that with an increase in electrolyte temperature the color of

the film becomes even whiter.

Adjustment and Correction of Electrolyte of the Bath

Oxidizing proceeds most completely in a strongly acid medium; therefore in the course of the work it is necessary to check the acidity of the bath more frequently by means of the determination of the hydrogen index (pH) of the electrolyte.

Certain works [3] indicate a need to maintain electrolyte pH strictly within the limits 1.5-2. The results of our tests showed that

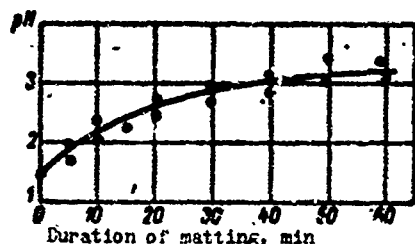


Fig. 5. The curve of the dependence of the pH of the bath electrolyte on the duration of oxidizing (τ).

a pH of 1.5-2 will be kept only in a freshly prepared solution and only during the initial 7-10 minutes of the oxidizing process (Fig. 5). In practice the process of oxidizing proceeds in an electrolyte whose pH is within the limits 2.5-3, since in the conditions of the anode process a deep change occurs in the composition of

the electrolyte (transition of tetravalent titanium into lower-valence forms). Due to this not only the pH of the electrolyte is changed, but also its color — from colorless to light brown. During prolonged storage and during mixing the light brown electrolyte again becomes colorless. During construction of the graph shown in Fig. 5, the pH of the electrolyte of the bath was determined every 10 minutes by two methods: with the help of universal indicator paper and the indicator "methyl-violet" (region of transition at $\text{pH} = 1-3$). The acid form is blue. As standards of comparison we used solutions with various values of pH. The change in bath pH was controlled according to the growth of time of the process and by its decrease. Such a method permits a more exact change of the electrolyte in the time of the process.

According to Fig. 5 it is possible to conclude that the correction of the electrolyte consists in maintaining the required value pH, 1.5-3, by means of a definite concentration of titanium salts. This is attained by the systematic addition of salts of titanium and oxalic acid, based on the calculated expenditure of these salts: $\text{TiO}(\text{KC}_2\text{O}_4)_2 \times 2\text{H}_2\text{O}$, 150-200 g/m²; $\text{H}_2\text{C}_2\text{O}_4$, 200 g/m². One can also use the results of periodic analyses of the oxidizing bath to maintain in it a titanium content of 1.5-2 g/liter [4].

The electrolyte of the bath must be systematically filtered, since slime [anode mud?] accumulates in it. One should not make large baths. The considerable evaporation of electrolyte at the operating temperature of 55° requires frequent addition of distilled water and hampers correction of the composition of the bath. With normal bath operation the service life of the electrolyte is composed of 60-70 amp-hr/liter.

Comparative Evaluation of Oxide-Films

The elasticity of mat films was tested on a special elasticity gage [4] and by bending on mountings with diameters of 10, 20, 30 and 40 mm. The results of the tests showed that mat film is more elastic than films obtained in sulfuric and oxalic acid electrolytes (Table 1). This is apparently explained by the comparatively high temperature of the electrolyte during matting and by the unique structure of the mat film.

The electrical insulating properties of mat film were tested by two methods: by measurement of the breakdown potential and of the resistivity of the film. The dielectric strength of the film was determined in a special attachment (Fig. 6). Factory tests of potentiometer frames showed that such a method gives a more correct (not

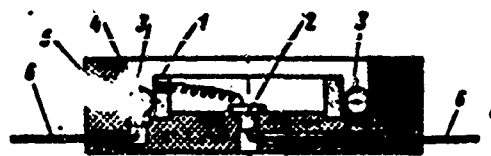


Fig. 6. Attachment for determination dielectric strength of anodized films. 1 - tested sample (frame of potentiometer), 2 - contact, 3 - spheres, 4 - textolite body of attachment, 5 - contact, 6 - conductor.

oversized) presentation of the magnitude of electrical strength than the accepted laboratory tests, contacting a small area of the tested surface.

The volume resistivity ρ_v of anodized films was determined on the instrument whose diagram is given in

Fig. 7. This instrument has electrodes for measurement of ρ_v of standard dimension (GOST 6433-52), which makes it possible to compare the obtained values of ρ_v of anodized films with

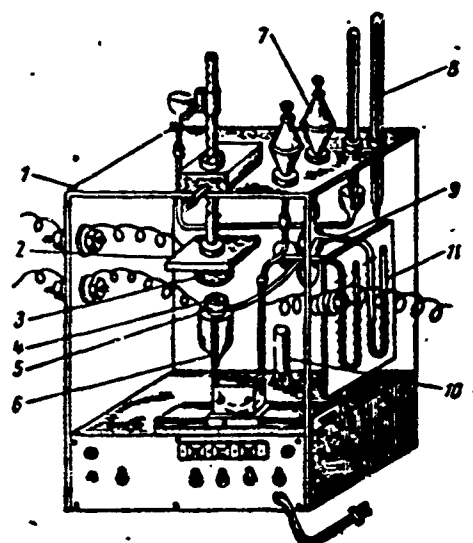


Fig. 7. Instrument for measurement of volume resistivity of anodized films by the method of direct deflection. 1 - test chamber, 2 - feed mechanism, 3 - high-potential electrode, 4 - measuring electrode, 5 - guard electrode, 6 - U-shaped tube with mercury, 7 - regulators of pressure of mercury, 8 - psychrometer, 9 - fan, 10 - electric heater, 11 - piezometers.

the handbook data for known dielectrics (textolite, ebonite, and others). Besides this, the guard electrode of the instrument permits more exact determination of the value of volume resistivity.

Comparative results of electrical properties of mat films are presented in Table 1.

Mechanical tests of samples

made of the alloys AD1, AMtsM, and D16-T with anodized films showed that tensile strength during extension of standard samples remained almost constant. The relative elongation of samples with mat film was much higher than that of films obtained by other methods of anodizing (see Table 1).

Table 1. Comparative Appraisal of Anodized Films

Name of anodizing process	Material of sample	Micro-hardness, kgf/mm ²	Elasticity (quantity of cracks on sample after 30-minute deformation)	Break-down voltage, V	Volume resistivity ρ_v in ohm-cm ³ (relative humidity 55%)	Mechanical properties		Roughness of anodized sample, per GOST 2789-59
						Tensile strength σ_B , kg/mm	Aspect ratio δ_H , %	
Matting, $i = 2$ a/dm^2 , $\delta = 12$	AMtsM	520-610	4	480	$4.6 \cdot 10^3$	Remains without change	42.3	V9
Ordinary sulfuric acid, $i = 1.5$ a/dm^2 , $\delta = 10 \mu$	AMtsM	260	12	310	$2.1 \cdot 10^{11}$	The same	25.4	V7
Ordinary oxalic acid	AMtsM	290	9	400	$4.1 \cdot 10^{12}$	"	27.1	7
Hard anodizing, $i = 2 a/dm^2$, $\delta = 70 \mu$	AMtsM	395	23	965	$1.2 \cdot 10^{14}$	"	16	6

Tests for abrasive wear were made on the instrument depicted in Fig. 8. Anodized tubular samples 3 were attached to both ends of rotor 2, driven by d-c electric motor 1. Glass tube 4, filled with

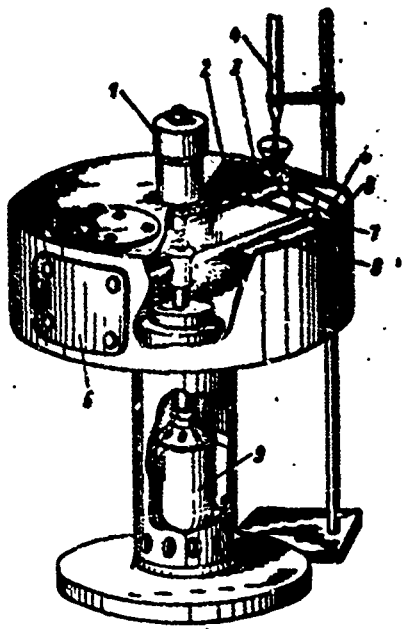


Fig. 8. Instrument for testing of anodized films for abrasive wear and friction wear. 1 - electric motor, 2 - rotor, 3 - tested tubular sample, 4 - glass tube, 5 - sample for friction test, 6 - cassette, 7 - steel sphere from anti-friction bearing, 8 - rotor, 9 - electric motor.

silicon carbide No. 80 in the form of abrasive particles, ends in a narrowed outlet, giving a constant, even flow of abrasive. Since two tested samples are placed in identical test conditions, this method permits reliable and rapid (2-3 minutes) comparison of the relative quality of films obtained under different conditions or by different methods. Tests were not conducted to full removal of the oxide films, in order to avoid wedging of particles of abrasive in the base metal.

In comparing the magnitude of abrasive wear (by loss of weight) of a mat film and an anodized film obtained by the method of hard anodizing, one can conclude that the mat film is more resistant to abrasive wear (Fig. 9). This is obviously explained by its higher hardness and plasticity as compared to the quite friable surface layer of the film obtained by the method of hard anodizing.

It is quite clear that the time of complete erosion of the hard oxide will be greater than that for the mat film, due to its greater thickness.

The resistance of the mat film to friction wear was tested on a machine of the Amsler type [Mi] (Mu) and on the instrument considered

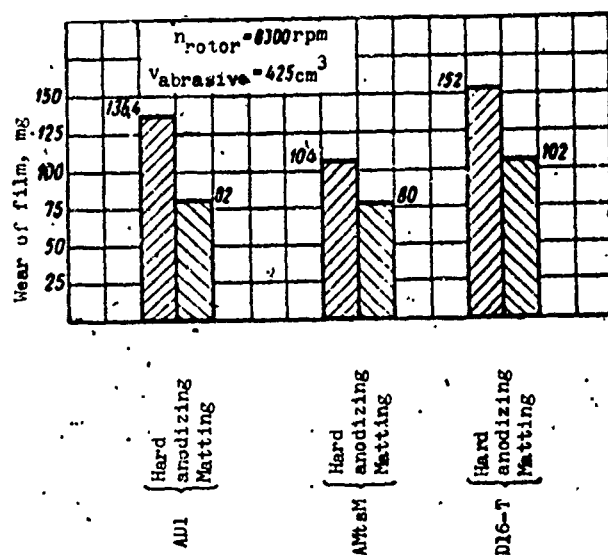


Fig. 9. Diagram of relative resistance to abrasive wear of mat film.

above (Fig. 8). Test samples 5 were placed in cassettes 6. Rotor 8 was actuated from d-c electric motor 9. Under the action of centrifugal force the spheres 7 in the tube emerged on the periphery of the sample, abrading it.

The results of the test showed that mat films resist friction wear considerably

better than sulfuric and oxalic acid films.

Conclusions

1. We studied the kinetics of growth mat film on the alloys AD1, D16-T, and AMtsM.
2. We studied the influence of the temperature of the solution on the kinetics of film growth.
3. We investigated the protective indices of mat films.
4. The magnitude of the pH of the electrolyte of the bath can be expanded to a value of 3 without damage to the quality of the film.
5. It has been established that mat films have a number of advantages as compared to oxide films formed in sulfuric and oxalic acid electrolytes, namely: mat films possess higher corrosion resistance, allowing their application on aluminum alloys for use in corrosive media and in media where high sanitation engineering requirements of the surface must be secured; these films possess high electrical strength and considerable electric volume resistivity, and hence can be recommended as insulators in instruments; mat films have higher hardness than sulfuric and oxalic acid films, being subject to

a smaller degree to friction wear and abrasive wear, and hence can be recommended as high-wear-resistant coatings for parts working briefly in a strongly corrosive medium.

6. Mat film is 8-10 times lighter than varnish and paint coatings and can be successfully used to replace them in instrument-making.

7. A deficiency of the considered method of matting is the rather high cost of the component parts of the electrolyte of the bath.

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